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Peculiar Band Gap Structure of Graphene Nanoribbons

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Abstract

Graphene nanoribbons are quasi-one-dimensional meterials with finite width. Characterizing a wide class of nanoribbons by edge shape and width, we make a systematic analysis of their electronic properties. The band gap structure of nanoribbons is shown to exhibit a valley structure with stream-like sequences of metallic or almost metallic nanoribbons. Among them, all zigzag nanoribbons are metallic, and armchair nanoribbons are metallic by period of 3. We find that these stream-like sequences correspond to equi-width curves, and that the band gap of chiral and armchair nanoribbons oscillate as a function of the width. Furthermore a possible application of nanoribbons to nanoelectronics is discussed.

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I. INTRODUCTION

Electronic properties of carbon systems are dramatically depend on their geometry and size. In particular, intensive research has been made on carbon nanotubes in the last decade. The large interest centers their peculiar electronic properties inherent to quasi-one-dimensional systems.

A similarly fascinating carbon system is a ribbon-like stripe of a graphite sheet, which is named graphene nanoribbons or carbon nanoribbons[1,2]. Recent experimental developments[3] enable us to isolate a graphene, which is a monolayer graphite. Nanoribbons have a higher variety than nanotubes because of the existence of edges. Though quite attractive materials, their too rich variety has made it difficult to carry out a systematic analysis of nanoribbons.

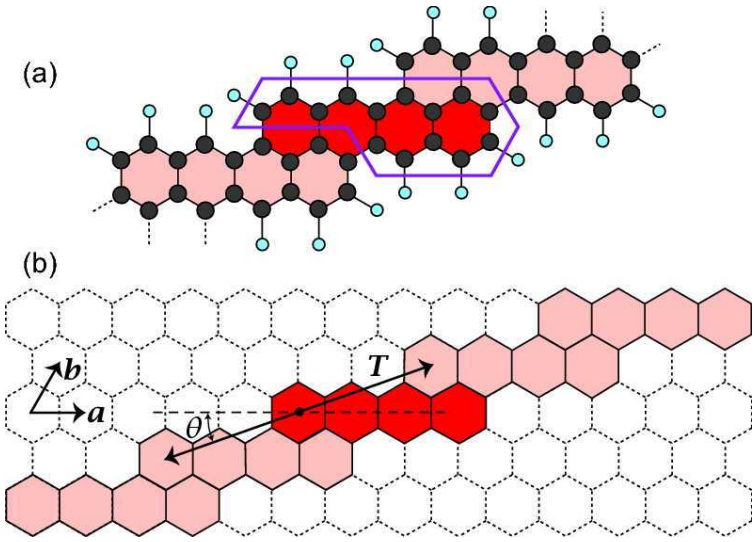

FIG. 1: (a) A typical structure of nanoribbons. A black circle stands for a carbon atom with one π electron, while a blue circle for a different atom such as a hydrogen. A closed area represents a unit cell. It is possible to regard the lattice made of black circles as a part of a honeycomb lattice. (b) A nanoribon is constructed from a chain of m connected carbon hexagons, as depicted in red, and by translating this chain by the translational vector $\mathbf{T} = \pm q\mathbf{a} + \mathbf{b}$ many times, as depicted in pink, where $q < m$. A nanoribbon is indexed by a set of two integers $\langle p, q\rangle$ with $p = m - q$. Here we have taken $m = 4$, $q = 2$, $p = 2$.

In this work, characterizing a wide class of nanoribbons by a set of two integers $\langle p, q\rangle$, we present a systematic analysis of their electronic property in parallel to that of nanotubes. They are shown to exhibit a rich variety of band gaps, from metals to typical semiconductors.

We reveal that there exist sequences of metallic or almost metallic nanoribbons which look like streams in valley made of semiconductors. They approach equi-width curves for wide nanoribbons. We also find a peculiar dependence of the electronic property of nanoribbons on the width w. Furthermore, we point out that the variety of nanoribbons make them promising candidates for electronic device applications.

II. CLASSIFICATION AND ELECTRONIC STRUCTURES OF GRAPHENE NANORIBBONS

The classification rule for the nanotubes says that it is metallic when $n_1 - n_2$ is an integer multiple of 3, and otherwise semiconducting, where (n_1, n_2) is a chiral vector of the nanotube. Suggested by this classification, as we illustrate in Fig.1, we consider a wide class of nanoribbons indexed by a set of two integers $\langle p, q\rangle$ representing edge shape and width. Nanoribbons with $q = 0$ possess zigzag edges, nanoribbons with $q = 1$ possess armchair edges and the other nanoribbons possess chiral edges.

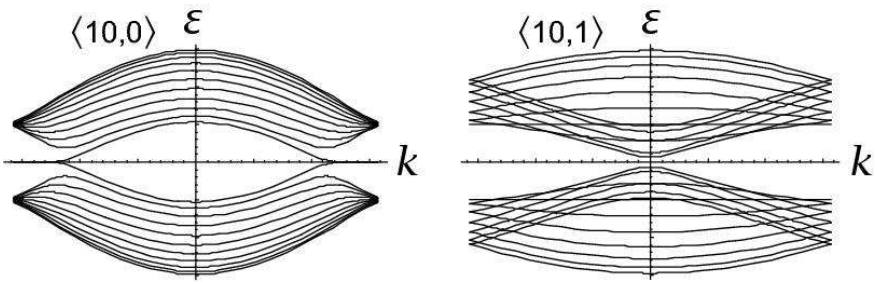

FIG. 2: The band structure of nanoribbons. The horizontal axis is the crystal momentum k, $-\pi < k < \pi$, while the vertical axis is the energy ϵ, $-3|t| < \epsilon < 3|t|$ with $|t| = 3.033$eV. The band structure depends strongly on the index q for fixed p, but depends on the index p only weakly for fixed q.

We carry out a systematic analysis of the electronic property of nanoribbons. It is well known that the electronic properties of graphene and nanotube are well explained by taking the nearest neighbor tight banding model. The analysis of nanoribbons can be done in a similar way. The tight-binding Hamiltonian is defined by

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle i,j\rangle} t_{ij} c_i^\dagger c_j, \tag{2.1}$$

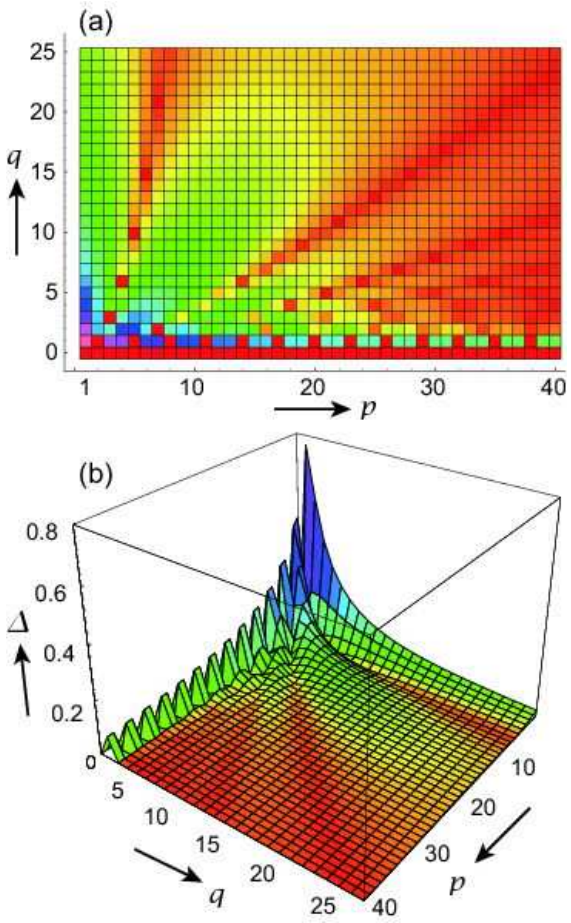

FIG. 3: The band gap structure of nanoribbons. (a) The horizontal and vertical axes represent the indices p and q, respectively. Magnitudes of band gaps are represented by colored squares. Redish (blue) gray squares represent small (large) gap semiconductors. Especially, metallic states are represented by red squares. (b) A bird's eye view. The vertical axis is the energy gap Δ in unit of $|t| = 3.033$eV. Nanoribbons make a valley structure with stream-like sequences of metallic points in the pq plane. We observe clearly three emergence patterns of metallic points: (a) All zigzag nanoribbons are metallic points. (b) Armchair nanoribbons with $p = 2, 5, 8, 11$, is metallic (c) Several sequences of metallic points on "streams" in valleys. In particular, nanoribbons are metallic on the points $\langle p, q\rangle$ with integers p and q with $q = p(p-1)/2$. They constitute the principal sequence of metallic points. Several sequences of metallic or almost metallic points are found in the valley of semiconducting nanoribbons. These sequences correspond to equi-width curves indexed by w as $p = -q + (w/2)\sqrt{(3(2q+1)^2+9)}$.

where ε_i is the site energy, t_{ij} is the transfer energy, and $c_i^\dagger$ is the creation operator of the π

electron at the site i. The summation is taken over the nearest neighbor sites $\langle i, j\rangle$. Carbon nanotubes are regarded as a periodic-boundary-condition problem, while carbon (graphene) nanoribbons are as a fixed-boundary-condition problem imposed on graphene.

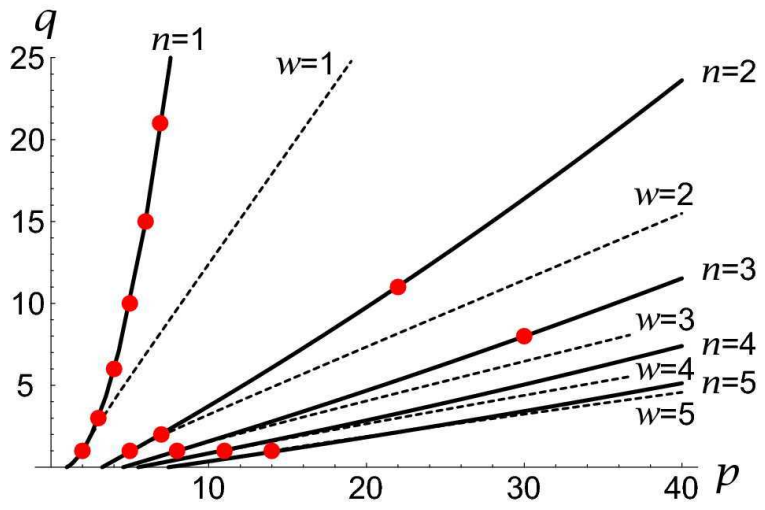

FIG. 4: Illustration of metallic points, sequences and equi-width curves. Metallic points are denoted by red circles. Solid curves represent sequences of metallic or almost metallic points, while dotted curves represent the points $\langle p, q\rangle$ possessing the same width. The width w is defined as $w = 2(p+q)/\sqrt{(3(2q+1)^2+9)}$. The n-th sequnce is tangent to the equi-width curve with $w = n$ at $q = 1$. These two curves become almost identical for sufficiently wide nanoribbons.

The band gap of nanoribbons is calculated for each point $\langle p, q\rangle$, as in Fig.2. Collecting all these results, we display the band gap structure in Fig.3. Nanoribbons exhibit a variety of properties in electronic conduction, from metals to typical semiconductors. It is remarkable that it makes a valley structure with stream-like sequences of metallic or almost metallic nanoribbons (Fig.3). It is observed that nanoribbons indexed by $\langle p, 0\rangle$ are metallic for all p, which are in the polyacene series with zigzag edges. Nanoribbons indexed by $\langle p, 1\rangle$ with $p = 2, 5, 8, 11, \cdots$ are found to be also metallic, which have armchair edges. This series has period 3, as is a reminiscence of the classification rules familiar for nanotubes.

We point out a peculiar dependence of the electronic property of nanoribbons on the width w, where

$$w = \frac{2\,(p+q)}{\sqrt{3\,(2q+1)^2+9}}. \tag{2.2}$$

We extract the stream curves out of Fig.3, and draw them in Fig.4. On this figure we

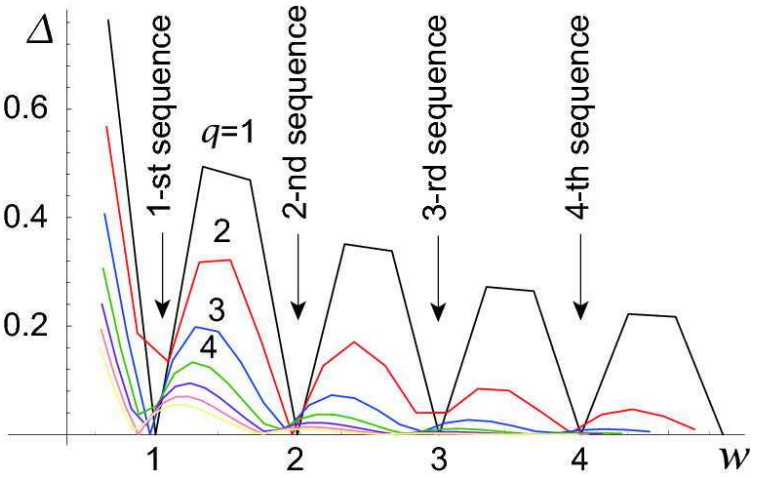

FIG. 5: The band gaps Δ in unit of $|t|$=3.033eV as a function of the width w. They oscillate and take local minima almost at the same values of the width w for any q. Their envelope decrease inversely against w.

also present equi-width curves. It is remarkable that these sequences and equi-width curves become almost identical for wide nanoribbons, as is clear in Fig.4. We have depicted the band gap as a function of the width w for each fixed q in Fig.5. The band gaps oscillate and the envelope of the band gap decreases inversely against w.

III. VAN HOVE SINGULARITIES

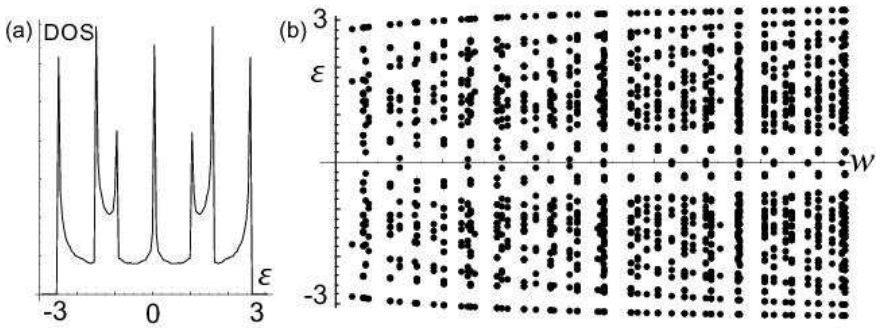

FIG. 6: (a) The density of state (DOS) of the $\langle 1,0\rangle$ nanoribbon. (b) Plot of van Hove singularities in the w-ε plane. For a given $\langle p,q\rangle$ nanoribbon, we calculate the width w and the energies ε at which van-Hove singularities develop. We have plotted the points (w,ε) for $q = 0, 1, 2, 3, 4$ and for all p in the region $w < 3$. A stripe pattern is manifest.

We calculate the energies ε at which van-Hove singularities develop due to the local band flatness at $k = 0$ for various $\langle p, q\rangle$ nanoribbons [Fig.6(a)]. Note that the optical absorption is dominant at $k = 0$ because the dispersion relation $\varepsilon = ck$ with c the light velocity. On the other hand the width w is determined by p and q as in (2.2). We show the energy ε of this peak as a function of w in Fig.6. A peculiar stripe pattern is manifest there. In particular, the maximum and minimum values take almost the same values $\pm 3\,|t|$, reflecting the electronic property of a graphite. The fact that there are on smooth curves present another justification to call w the width of nanoribbon.

IV. DEVICES

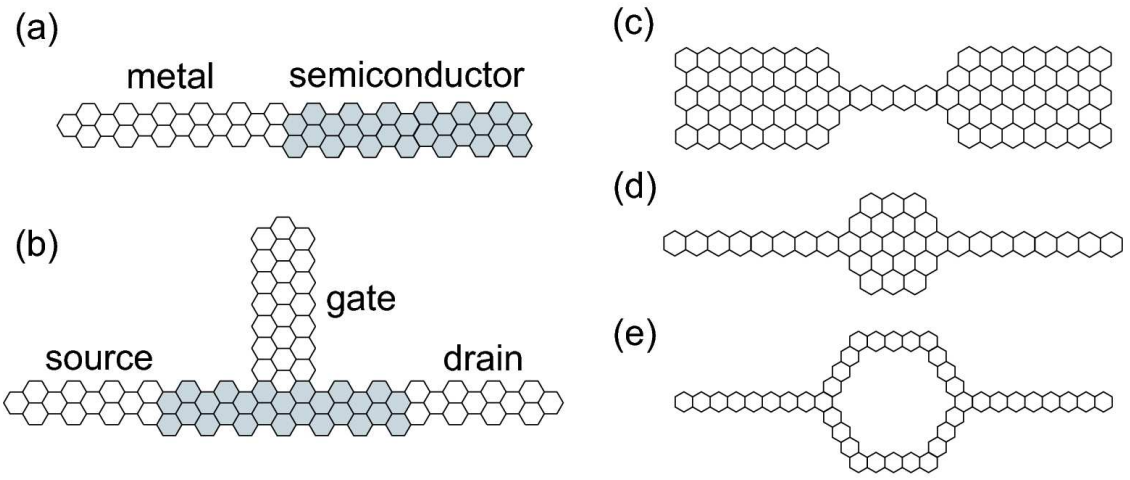

FIG. 7: Several possible nanoribbon devices. (a) Metal-semiconductor hetro-junction of nanoribbons with different indices (Schottky diode). (b) Hetro-junction of nanoribbons with transistor configuration (Schottky gate field effect transistor). (c) Point contact. (d) Quantum dot. (e) Aharonov-Bohm ring.

We have revealed a rich variety of band gaps in graphene nanoribbons. They are either quasi-one-dimensional metals or semiconductors depending on their edge shape and width. Graphene nanoribbons could be promising candidates of molecule devices, similarly to nanotubes[4], because of ballistic transport at room temperature.

We mention the merits of nanoribbons in comparison to nanotubes. Two nanoribbon

segments with different atomic and electronic structures can be seamlessly fused together to create intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions without introducing a pentagon and a heptagon into the hexagonal carbon lattice. Diodes or transistors could be made of nanoribbons, as illustrated in Fig.7. For instance, a metal-semiconductor junction makes Schottky barrier and may behave like a Schottky diode. Similarly Schottky gate field-effect transistor, point contact, quantum dot and Aharonov-Bohm ring may be realized. We might even design a complex of electronic circuits by etching a monolayer graphite in future. It is interesting problems to calculate electronic characteristics of various junctions, which will be studied elsewhere.

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